

DRAWINGS ATTACHED

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(54) METHOD FOR SEPARATING CARBON DIOXIDE
FROM OTHER GASES

(71) We, MINE SAFETY APPLIANCES COMPANY, a corporation organized under the laws of the Commonwealth of Pennsylvania, United States of America, of 201 North Braddock Avenue, Pittsburgh, Pennsylvania 15208, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the separation of carbon dioxide from other gases and more particularly to a method in which carbon dioxide is sorbed from a mixture of gases on a weak base ion exchange resin and desorbed from the resin with steam.

Carbon dioxide is separated from gas mixtures in the manufacture of carbon dioxide, as in sorption from flue gases resulting from burning of carbonaceous materials, as well as in a variety of situations in which the primary purpose of the separation is to remove carbon dioxide from a desired product gas. Thus carbon dioxide is removed from process gases or synthesis gas in steam-hydrocarbon reforming methods of producing hydrogen, ammonia and methanol. Carbon dioxide is also removed from gaseous air-hydrocarbon combustion products to produce oxygen- and carbon dioxide-free inert gas atmospheres, for example in providing inert atmospheres for fruit and produce storage. And, in providing habitable atmosphere to chambers such as submarines and space capsules, exhaled carbon dioxide must be removed from the atmosphere.

In accordance with this invention, a gas mixture containing carbon dioxide is contacted with a bed of weakly basic ion exchange resin that sorbs carbon dioxide and the carbon dioxide is subsequently desorbed and the resin bed regenerated by condensing steam in the bed beginning at one end of the bed and progressing through the entire bed. The steam regeneration procedure sequentially elutes from the bed first the non-sorbed gases other than carbon dioxide that are retained in the free space of the bed and second the desorbed carbon dioxide. This mode of regeneration provides a higher purity of carbon dioxide and carbon dioxide-free gas and constitutes a primary feature of this invention.

The method is suitable for separating carbon dioxide from gas mixtures containing air, inert gases such as helium, neon and argon, diatomic permanent gases such as hydrogen, oxygen and nitrogen, and other non-acid gases that are not sorbed by the weak base ion exchange resins. Gas mixtures containing acid gases such as sulfur oxides in flue gases, can be pretreated by conventional methods to remove the acid gas prior to their introduction to the carbon dioxide separation process.

Fig. 1 shows partly in section and partly schematic an apparatus for performing the method of this invention;

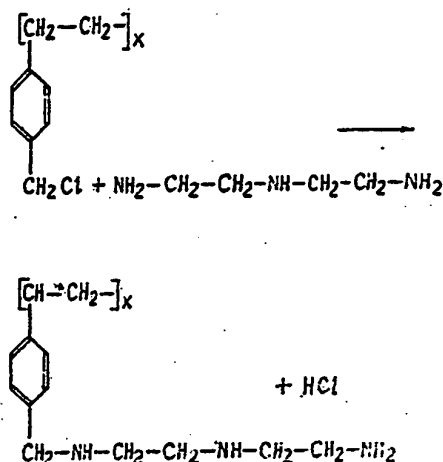
Fig. 2 schematically illustrates the condition of the resin bed of Fig. 1 during a regeneration cycle.

Weakly basic ion exchange resins are generally suitable for use as an sorbent in the practice of this invention. Such resins have primary, secondary and/or tertiary amine functionally active groups attached to a polymeric matrix. The polymeric matrix may conventionally be polystyrene, polystyrene-divinylbenzene copolymer, phenol-formaldehyde, polyacrylic acid, polymethacrylic acid-divinylbenzene copolymer, or an epoxide type polymer. A large number of such resins are commercially available and are usable in this invention, with varying degrees of suitability.

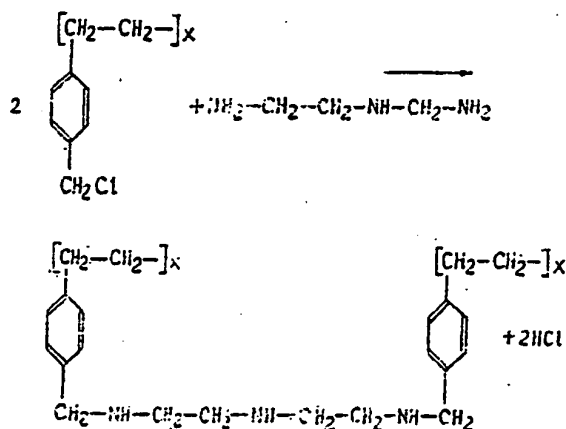
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Preferred weakly basic ion exchange resins, that have an especially high affinity and capacity for carbon dioxide and may be repeatedly regenerated without substantial impairment of sorption characteristics, include those resins in which the active group has polyamine functionality and contains at least one secondary amine-nitrogen. Such materials are prepared by the reaction of addition or condensation polymers with polyfunctional amines having a secondary amine nitrogen such as, for example, diethylenetriamine, triethylenetetramine and tetraethylenepentamine. Such preferred resins include polyacrylic acid-polyamine resins prepared according to U.S. Patent 2,582,194 and epoxide-polyamine resins that are conventionally prepared by reaction of an epoxide resin and a polyamine in a solvent such as xylene.

Polystyrene-divinylbenzene copolymer gel type resins having polyamine functional groups are especially preferred absorbents. Resins of this type may be prepared by reaction of chloromethylated styrene-divinylbenzene copolymer with an amine such as diethylenetriamine, triethylenetetramine, tetraethylenepentamine and other polyfunctional amines. An equimolar, or in excess thereof, amount of amine for each chloromethyl group forms condensation of one chloromethyl group with one amine group as illustrated by the reaction using diethylenetriamine:



If the proportion of amine is about one-half of equimolar, condensation providing additional crosslinking and predominantly secondary amine functionality according to the following equation is favored:



The carbon dioxide capacity of this type resin correlates to the ion exchange capacity and conventional methods of improving ion exchange capacity also improves the dynamic carbon dioxide capacity. Thus, for example, to provide suitable porosity, it is

generally preferred to use copolymers containing less than about 10% divinylbenzene, suitably 3—5%. Amberlite (Registered Trade Mark) IR-45, a chloromethylated polystyrene-divinylbenzene copolymer aminated with diethylenetriamine, is a typical commercially available resin of the preferred type.

The method is further described in reference to Fig. 1 which illustrates, partly in schematic, an apparatus for removing expired CO₂ from air in closed room for the maintenance of a habitable atmosphere. A bed 2 of weakly basic ion exchange resin is contained between screens 4 in a chamber 6 formed of a housing 8 having removable end closures 10 secured with flanges 12. A layer of flexible open cell foam 13 accommodates changes in the bed volume caused by the differing degree of swelling of the resins with differing water content. The chamber is provided with an air inlet 14, outlet 15, steam inlet 16 and carbon dioxide outlet 27 together with associated valves 20, 22, 24 and 26. Thermal switches 30 and gas volume totalizer 32 are connected with appropriate circuitry to open and close control valves as will be described in detail later. Condenser 29 removes water vapor from the discharged air when dehumidification is desired, as is the case in maintaining a respirable atmosphere.

With valves 24 and 26 closed and valves 20 and 22 open, room air containing carbon dioxide is forced through the resin bed by blower 34, whereby carbon dioxide is sorbed by the resin. The sorption cycle may be of a predetermined length of time dependent on the design characteristics of the particular apparatus, or it may be terminated by response to a signal generated by detection of CO₂ in the outlet gases using conventional gas analysis control systems.

The resins to be effective in sorbing carbon dioxide contain sorbed water, suitably above about a 5% water content; preferably however the resin is not wet with unsorbed water, which hinders carbon dioxide absorption. The capacity of various resins differs somewhat but generally a water content of below about 30% is substantially entirely sorbed water. The humidity of the gas being passed through the resin bed is adjusted, if necessary, to provide a suitable equilibrium water content in the resin. At 75°F., for example, a gas with a relative humidity of 50% will equilibrate at about 5—10 wt. percent water in the resin, while a gas with 90% relative humidity will equilibrate with a 25—30% resin water content. It is generally preferred to use a gas having a 75—90% relative humidity.

Carbon dioxide is readily sorbed by the resin beds at ordinary ambient or room temperatures, and higher and lower temperatures may be used if desired. Sorption efficiency is increased somewhat at lower temperatures above the freezing point of water, while sorption efficiency is substantially reduced at temperatures above about 90°F. It is generally preferred to operate the sorption cycle at a convenient temperature between about 40—90°F. Temperature adjustment may be obtained by jacketing the chamber containing the resin bed for heating or cooling or, more conveniently, by adjusting the temperature of the input gas.

When used to remove carbon dioxide for the purpose of maintaining habitable atmosphere, the input gas will contain about 0.4 to 0.5% carbon dioxide. As the sorption cycle commences, the effluent from the resin bed will contain very little carbon dioxide, for example, about 0.1% or less CO₂, the amount depending on bed depth, space flow velocities, the particular resin used and other parameters according to conventional sorption principles. As the sorption cycle proceeds, the effluent will contain a slowly increasing amount of carbon dioxide and when the effluent reaches a predetermined carbon dioxide concentration the sorption cycle is terminated. In the case of maintaining habitable atmospheres, the sorption cycle is preferably terminated when the effluent contains about 0.2—0.25% carbon dioxide; at these input and effluent carbon dioxide concentrations, the resins will sorb between about 1.75 and 2.25% carbon dioxide by weight. At higher carbon dioxide concentrations, a larger amount of carbon dioxide is sorbed, for example, with 2% input and 1.5% output carbon dioxide concentration, the resins sorb about 4% by weight of carbon dioxide.

In accordance with this invention, the sorbed carbon dioxide is displaced from the resin bed by introducing steam to the bed while at the low temperature used in the sorption cycle, suitably below about 90°F., whereby steam condenses and the condensed steam is sorbed on the resin transferring the latent heat of vaporization to the resin. As steam is introduced and condenses on the sorbent, a front of condensing steam proceeds lengthwise through the bed displacing sorbed carbon dioxide and air contained in the free space of the bed. Because of the increase in partial pressure of CO₂ ahead of the condensing front, CO₂ is resorbed so that the air originally in the bed is eluted more rapidly than the CO₂.

The regeneration method provides an effective separation of the desorbed carbon

dioxide and displaced air, as is explained in detail with reference to Fig. 2. Fig. 2 schematically represents the conditions of a resin bed 36 during regeneration when the condensing front has reached position 38. When steam is introduced at one end of the bed, it will condense on and heat the cooler resin bed, simultaneously displacing air, while the steam pressure drops at the condensing front. The upstream steam pressure pushes more steam past the hot wet surface into contact with more cool bed material. The gas mixture proceeding through the bed is steam, desorbed carbon dioxide and air. The steam condenses in the condensation zone 1. The hot carbon dioxide-air mixture passing from the condensation zone is cooled by the bed in zone 2. The carbon dioxide concentration is quite high in this region and the high partial pressure causes the carbon dioxide to be rapidly resorbed by the resin in amounts approaching the theoretical capacity of the resin, up to about 20% carbon dioxide by weight at 1 atmosphere of carbon dioxide pressure. The displaced air is not sorbed so it passes to zone 3 and is first discharged from the bed outlet 40. When the leading edge of zone 2 reaches the end of the bed, suitably determined by measuring the volume of gas displaced or an increase in temperature to about 90°C., some CO₂ will pass from the bed with the displaced air. Sequentially, when the condensing front approaches the downstream end of the resin bed, suitably determined by a further increase in temperature, carbon dioxide only is eluted. A feature of this regeneration mode is the self-correcting character of steam flow through the packed bed, thus minimizing channeling. Wherever there are sites in the bed which are cold, these sites act as condensation points with the water serving to increase the pressure drop. This forces steam to be condensed elsewhere such that the bed has a very uniform temperature in any cross-sectional plane.

Now with reference to Fig. 1, valve 20 is closed and the regeneration is commenced by opening valve 24 which allows steam to enter the bed at a predetermined rate so that it condenses progressively through the bed as previously described. The displaced air first eluted from the resin bed is discharged through valve 22 and returned to the room air chamber through condenser 29.

When the condensing front advances through the bed to the extent that the downstream side of the resorption zone reaches the end of the resin bed, carbon dioxide will begin to be desorbed and eluted from the bed. Valve 22 is then closed and valve 26 opened to discharge the carbon dioxide through conduit 27. The valves may be automatically operated to commence the regeneration cycle in response to a signal generated by detection of carbon dioxide in the effluent gases. Preferably, during the regeneration cycle the valves are operated in response to a volume totalizer 32, which closes valve 26 and opens valve 28 through a suitable relay system. This volume totalizer is adjusted to signal when the volume of gas eluted corresponds to the volume of air originally in the bed.

Thermal switch 30 closes at about 210—212°F., or at the arrival of the condensing front, and actuates suitable relays to close the steam valve 24 and valve 26, thus ending the regeneration cycle.

Depending on whether the primary objective is to recover pure carbon dioxide or to remove carbon dioxide from other gas, the time of closing valve 22 and opening valve 26 can be adjusted to provide either a discharge through valve 26 substantially completely free of carbon dioxide or a discharge through valve 27 of carbon dioxide substantially completely free of the other gas. Up to about 85% of the carbon dioxide or other gas can be cleanly separated at a purity of 99+%, and higher recoveries are possible if some contamination is permissible.

Blower 34 is then turned on, and valves 20 and 22 are opened to commence the next sorption cycle. The air flow through the bed cools it rapidly and elutes excess water remaining in the resin from the regeneration cycle, which is then removed from the air stream by condenser 29.

The regeneration method that separates air and carbon dioxide is a significant and valuable feature whether the object of the separation is to recover either carbon dioxide or the air or other non-sorbed gas. For example, in life support systems in space where dumping of air left in the bed is costly, the separation of CO₂ by our regeneration method permits the segregated carbon dioxide to be dumped while retaining substantially all the air.

Illustrative of the effectiveness of this invention, in a run using the apparatus of Fig. 1, 20 cfm of room air (80°F.) containing 0.48% CO₂ was passed through a bed of Amberlite Registered Trade Mark IR-45 resin 15 inches in diameter and 5 1/2 inches deep, and weighing 25.8 pounds. After 1 hour, the bed had sorbed 0.5 pounds of CO₂. The effluent gas contained less than 0.01% CO₂ for a further 30 minutes, and then rose to 0.28% at the end of the hour. Steam was then admitted to the end of the

bed at the rate of 9 pounds per hour. After about 7 minutes the temperature of thermal switch 30 reached 90°F., whereupon the effluent air return to the chamber was terminated and the effluent was directed through CO₂ outlet 27; at this point about 95% or 6.7 cu. feet, of the air in the bed had been discharged with virtually no elution of carbon dioxide. After about 6 more minutes thermal switch 30 reached 210°F. operating to stop the steam flow, close valve 27 and commence a repeat of the sorption cycle. The carbon dioxide was substantially completely desorbed and recovered. The excess water remaining in the resin bed was eluted from the bed after about 5 minutes of air flow in the next following sorption cycle. The absorption-regeneration cycle can be repeated for an indefinite number of cycles in excess of 1,000 without any significant change in performance.

In our co-pending Application No. 31344/70 (Serial No. 1296888) we have described and claimed a method of separating carbon dioxide from mixtures with non-acid gases comprising the steps of contacting said gas mixture at a first carbon dioxide partial pressure with a weakly basic ion exchange resin whereby carbon dioxide is sorbed by said resin, and reducing the carbon dioxide partial pressure of the gas in contact with said resin to a second partial pressure whereby carbon dioxide is desorbed from said resin.

WHAT WE CLAIM IS:—

1. A method of separating carbon dioxide from a mixture of non-acid gases comprising the steps of passing said mixture through a bed of weakly basic ion exchange resin at a temperature at which the carbon dioxide is sorbed by said resin, said bed having an inlet and an outlet end, introducing steam to said inlet end under such conditions that the steam condenses at the inlet end and a front of condensing steam proceeds lengthwise through the bed, whereby displaced non-sorbed gas and desorbed carbon dioxide are sequentially eluted from the bed.
2. A method according to claim 1 in which the resin has amine polyfunctionality and at least one secondary amine nitrogen.
3. A method according to claim 2 in which the polymeric matrix of said resin is a polystyrene-divinylbenzene copolymer.
4. A method according to claim 1, 2 or 3, in which the said gas mixture is at a temperature between 40°F. and 90°F. and has a relative humidity between 75% and 90%.
5. A method of removing carbon dioxide from breathable atmosphere in a closed chamber comprising the steps of passing atmosphere from said chamber through a bed of weakly basic ion exchange resin at a temperature at which carbon dioxide is sorbed by said resin and returning atmosphere effluent from said bed to said chamber, said bed having an inlet end and an outlet end; stopping said air flow when the carbon dioxide content of said effluent air reaches a predetermined concentration; introducing steam to said inlet end under such conditions that the steam condenses at the inlet end and a front of condensing steam proceeds lengthwise through the bed whereby breathable atmosphere and carbon dioxide are sequentially eluted from said bed and said bed is regenerated; returning the said eluted atmosphere to said chamber and discharging said eluted carbon dioxide outside said chamber.
6. A method according to claim 5 in which the resin has polyamine functionality and at least one secondary amine nitrogen.
7. A method according to claim 6 in which the polymeric matrix of said resin is a polystyrene-divinylbenzene copolymer.
8. A method according to claim 7 in which the amine component of said resin is diethylenetriamine.
9. A method according to any of claims 5 to 8, in which the air is at a temperature between 40°F. and 90°F. and has a relative humidity between 75% and 95%.
10. A method of separating carbon dioxide from a mixture of non-acid gases, substantially as described with reference to the accompanying drawings.

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